Supplementary Information

A HPLC-MS method for profiling triterpenoid acids and triterpenoid esters in *Osmanthus fragrans* fruits

Xiaoyan Liao, a,b Fangli Hu a and Zilin Chen *a,b

*a Key Laboratory of Combinatorial Biosynthesis and Drug Discovery (Ministry of Education), and School of Pharmaceutical Sciences, Wuhan University, Wuhan 430071, China*

*b State Key Laboratory of Transducer Technology, Chinese Academy of Sciences, Beijing 10080, China*

*Corresponding Author*

Zilin Chen. E-mail: chenzl@whu.edu.cn

Tel.: +86 27 68759893; fax: +86 27 68759850.

E-mail addresses of other authors:

liao.xy@whu.edu.cn (Xiaoyan Liao)

2713656602@qq.com (Fangli Hu).
Fig. S1. MS² spectra of compounds E1-E31
Compounds E6: m/z 487.4

Compounds E7: m/z 487.4

Compounds E8: m/z 487.4

Compounds E9: m/z 649.4

Compounds E10: m/z 649.4
Compounds **E16**: m/z 663.4

Compounds **E17**: m/z 471.4

Compounds **E18**: m/z 471.4

Compounds **E19**: m/z 633.4

Compounds **E20**: m/z 471.4
Compounds **E30**: m/z 455.4

Compounds **E31**: m/z 455.4

Compounds **E6α**: m/z 487.4

Compounds **E6β**: m/z 487.4

2-epitormentic acid: m/z 487.4
**Table S1** HPLC-MS/MS parameters for semi-quantitative determination of triterpenoid acids and triterpenoid esters

<table>
<thead>
<tr>
<th>Q1 (m/z)</th>
<th>Q3 (m/z)</th>
<th>CE (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>455.4</td>
<td>455.4*</td>
<td>-10</td>
</tr>
<tr>
<td></td>
<td>409.4</td>
<td>-55</td>
</tr>
<tr>
<td></td>
<td>407.4</td>
<td>-55</td>
</tr>
<tr>
<td>471.4</td>
<td>471.4*</td>
<td>-10</td>
</tr>
<tr>
<td></td>
<td>453.4</td>
<td>-40</td>
</tr>
<tr>
<td></td>
<td>423.4</td>
<td>-55</td>
</tr>
<tr>
<td></td>
<td>405.4</td>
<td>-60</td>
</tr>
<tr>
<td></td>
<td>393.4</td>
<td>-60</td>
</tr>
<tr>
<td></td>
<td>377.4</td>
<td>-68</td>
</tr>
<tr>
<td>487.4</td>
<td>487.4*</td>
<td>-10</td>
</tr>
<tr>
<td></td>
<td>469.4</td>
<td>-40</td>
</tr>
<tr>
<td></td>
<td>427.4</td>
<td>-55</td>
</tr>
<tr>
<td></td>
<td>425.4</td>
<td>-35</td>
</tr>
<tr>
<td></td>
<td>423.4</td>
<td>-55</td>
</tr>
<tr>
<td></td>
<td>409.4</td>
<td>-50</td>
</tr>
<tr>
<td>503.4</td>
<td>503.4*</td>
<td>-10</td>
</tr>
<tr>
<td></td>
<td>485.4</td>
<td>-40</td>
</tr>
<tr>
<td>617.4</td>
<td>617.4</td>
<td>-10</td>
</tr>
<tr>
<td></td>
<td>497.4</td>
<td>-60</td>
</tr>
<tr>
<td></td>
<td>145.0*</td>
<td>-60</td>
</tr>
<tr>
<td>633.4</td>
<td>633.4</td>
<td>-10</td>
</tr>
<tr>
<td></td>
<td>497.4</td>
<td>-60</td>
</tr>
<tr>
<td></td>
<td>161.0*</td>
<td>-60</td>
</tr>
<tr>
<td></td>
<td>145.0*</td>
<td>-60</td>
</tr>
<tr>
<td>Compound</td>
<td>Calibration curve</td>
<td>Linear range *</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>E1</td>
<td>$Y=2130492.7x-1566.6$</td>
<td>0.05-1</td>
</tr>
<tr>
<td>E2</td>
<td>$Y=712231.1x-1783.8$</td>
<td>0.05-1</td>
</tr>
<tr>
<td>E3</td>
<td>$Y=602469.1x+4578.6$</td>
<td>0.05-1</td>
</tr>
<tr>
<td>E4</td>
<td>$Y=453981.9x+2698.3$</td>
<td>0.05-1</td>
</tr>
<tr>
<td>E5</td>
<td>$Y=1533955.8x+4128.0$</td>
<td>0.05-1</td>
</tr>
<tr>
<td>E6</td>
<td>$Y=38354251.4x-42850.3$</td>
<td>0.005-0.2</td>
</tr>
<tr>
<td>E6b</td>
<td>$Y=280036.6x+1771.1$</td>
<td>0.01-0.5</td>
</tr>
<tr>
<td>E7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E8</td>
<td>$Y=388114.6x+1580.6$</td>
<td>0.05-1</td>
</tr>
<tr>
<td>E9</td>
<td>$Y=640750.8x+1456.0$</td>
<td>0.01-1</td>
</tr>
<tr>
<td>E10</td>
<td>$Y=2607369.1x+12217.8$</td>
<td>0.01-1</td>
</tr>
<tr>
<td>E11</td>
<td>$Y=14795606.0x-51202.0$</td>
<td>0.005-0.3</td>
</tr>
<tr>
<td>E12</td>
<td>$Y=75990617.5x+432609.9$</td>
<td>0.005-0.3</td>
</tr>
<tr>
<td>E13</td>
<td>$Y=4785408.6x+7685.4$</td>
<td>0.001-0.5</td>
</tr>
<tr>
<td>E14</td>
<td>$Y=18026.0x+344.1$</td>
<td>0.1-1</td>
</tr>
<tr>
<td>E15</td>
<td>$Y=10483746.4x+65745.3$</td>
<td>0.001-0.3</td>
</tr>
<tr>
<td>E16</td>
<td>$Y=29406.6x+670.8$</td>
<td>0.1-1</td>
</tr>
</tbody>
</table>

* Semi-quantitative ions

**Table S2** Method validation for semiquantitative determination of triterpenoid acids and triterpenoid esters by HPLC-MS.
<table>
<thead>
<tr>
<th></th>
<th>Equation</th>
<th>R²</th>
<th>Dilution Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>E17</td>
<td>Y = 37310466.2x + 262841.7</td>
<td>0.9978</td>
<td>-</td>
</tr>
<tr>
<td>E18</td>
<td>Y = 1365534.6x + 1523.0</td>
<td>0.9996</td>
<td>1.1</td>
</tr>
<tr>
<td>E19</td>
<td>Y = 18939136.2x + 76312.4</td>
<td>0.9992</td>
<td>0.7</td>
</tr>
<tr>
<td>E20</td>
<td>Y = 244012.5x + 795.1</td>
<td>0.9989</td>
<td>4.3</td>
</tr>
<tr>
<td>E21</td>
<td>Y = 4310168.1x + 23628.9</td>
<td>0.9990</td>
<td>4.8</td>
</tr>
<tr>
<td>E22</td>
<td>Y = 845150.2x + 7491.6</td>
<td>0.9987</td>
<td>4.0</td>
</tr>
<tr>
<td>E23</td>
<td>Y = 5805087.2x + 28232.9</td>
<td>0.9989</td>
<td>4.6</td>
</tr>
<tr>
<td>E24</td>
<td>Y = 1337238.3x - 2687.9</td>
<td>0.9998</td>
<td>4.0</td>
</tr>
<tr>
<td>E25</td>
<td>Y = 9798596.1x + 16690.1</td>
<td>0.9998</td>
<td>4.2</td>
</tr>
<tr>
<td>E26</td>
<td>Y = 2716866.9x - 4301.2</td>
<td>0.9996</td>
<td>4.9</td>
</tr>
<tr>
<td>E27</td>
<td>Y = 1947993.0x + 4019.2</td>
<td>0.9997</td>
<td>2.2</td>
</tr>
<tr>
<td>E28</td>
<td>Y = 116209063.4x + 328435.1</td>
<td>0.9974</td>
<td>0.6</td>
</tr>
<tr>
<td>E29</td>
<td>Y = 30427012.2x + 60729.0</td>
<td>0.9982</td>
<td>1.0</td>
</tr>
<tr>
<td>E30</td>
<td>Y = 3180698.7x + 8243.7</td>
<td>0.9998</td>
<td>3.5</td>
</tr>
</tbody>
</table>

* Dilution rate